Journal of Statistical Physics, Vol. 80, Nos. 3/4, 1995

Twist in an Exactly Solvable Directed Lattice Ribbon

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Received January 24, 1995; final February 14, 1995

We investigate the transition between a twisted regime and a disordered regime in a directed ribbon model on a cubic lattice. A fugacity corresponding to an interaction which models half-twists in the ribbon is introduced and the interacting model is solved exactly. Our results suggest that conformational entropy and a local interaction which induces twist are key ingredients to model qualitatively the crossover behavior between a twisted (helical) regime and a denatured regime in duplex biopolymers such as DNA.

KEY WORDS: Ribbon; lattice models; twist in DNA.

1. INTRODUCTION

The traditional model of the conformational properties of linear polymers in dilute solution is the self-avoiding walk,[1,2] i.e., a one-dimensional piecewise linear curve on a lattice, subjected to particular geometrical constraints (self-avoidance). In spite of its simplicity, this model captures several of the essential features which determine the large-scale properties of such molecules and has been adapted to include attractive forces (to model collapse in polymers), closed to form a ring (to examine topological features such as knotting), and extended to a variety of related models relevant to branched polymers. However, some biologically important polymers such as duplex DNA and RNA exist as double-stranded molecules. where the two strands of complementary nucleotides are wound as right-handed helices around each other and around a common axis.

It is believed that the duplex structure of DNA is needed to maintain the fidelity of a long genetic message.[3,4] In nature, the helix is the most commonly occurring structure found in folded proteins, and this

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0022-4715/95/0800-0781$07.50/0

observation extends to RNA and DNA. Such helical structures allow monomers in the linear molecules to align in space into energetically favorable conformations, at the cost of conformational entropy.[4]

The thermodynamic description of the conformational properties of these polymers entails a free energy minimum that selects the helical structures in proteins, RNA, and DNA. In DNA, this free energy minimum is obtained by a double helix, at the price of a loss of conformational degrees of freedom, compensated for by interactions between monomers which are repeating along the two strands. This overcomes the conformational entropy at low temperatures, but a higher temperatures it is found that the free energy minimum favors a disordered regime; the molecule becomes untwisted and it is called denaturated.

A model which has proved useful in modeling the double-helical structure of DNA is the continuum ribbon model[5,6] in which the hydrogen bonds between the nucleotides of the two strands form an orientable ribbon surface whose boundary is precisely the two backbone strands. In this picture the winding of the two strands corresponds to the twisting of the ribbon. In other words, the interactions between repeating structures in base pairs in the molecule induce a local twist in the ribbon counterpart.

These factors can be modeled by a lattice ribbon model for DNA.[7] The lattice ribbon will have conformational entropy due to both local degrees of freedom and global conformations. A fugacity which acts locally along the ribbon will represent the interaction between repeating units along the polymer chain. Of course, the correspondence between the physical nature of DNA and the lattice ribbon model is only qualitative; we expect to model the behavior of real biopolymers only at a qualitative level. The lattice ribbon model has several advantages. In the first instance, we can use techniques from the theory of self-avoiding walks to prove some results involving asymptotic behavior.[2] In the second instance, we are interested in an exactly solvable model, and a directed version of a lattice ribbon (analogous to a directed walk model[8,9]) will prove to be appropriate in this case.

In this paper we construct a directed lattice ribbon model with a local interaction which induces half-twist on a local scale in the ribbon. We solve the model and investigate its thermodynamic properties. In our model an ordered, helical regime with low conformational entropy is found at low temperatures, while a disordered regime is found at high temperatures. We organize the paper as follows: In Section 2 we introduce the directed ribbon model and find its generating function. The analytic structure of the generating function and the thermodynamics of the model are discussed in Section 3. We conclude the paper in Section 4 with a few comments about our results.

2. DESCRIPTION OF THE MODEL AND GENERATING FUNCTION

We shall be concerned with the simple cubic lattice $\mathscr{Z}^3$ and we define a plaquette as a unit square, with vertices with integer coordinates. We can build a ribbon by taking a plaquette and appending a second plaquette on one of its edges. A new plaquette is appended onto an edge of the last plaquette, and the process is repeated while the ribbon grows in length. The first and last plaquette in a ribbon are adjacent to only one plaquette in the ribbon; we say that they have degree 1. On the other hand, the intermediate plaquettes in the ribbon are adjacent to two neighbors and have degree 2. Edges in the ribbon shared with two plaquettes are called *ribbon edges*, and those incident with only one plaquette are called *boundary edges*.

Let $\{\hat{\imath}, \hat{\jmath}, \hat{k}\}$ be the canonical unit vectors in $\mathscr{Z}^3$. Suppose that R is a ribbon and let the maximal coordinate of the ribbon in the $\hat{k}$ direction be M. Suppose also that the last plaquette in the ribbon has maximal coordinate M. Then the last plaquette has at least one edge in the plane $z = M$. We also suppose that at least one of these edge, where we can append a new plaquette to continue the ribbon. We use the following rules in continuing the construction of this ribbon: Any new plaquettes are added onto a boundary edge of the last plaquette, and either this addition increases the maximal coordinate M in the $\hat{k}$ direction or the plaquette is added in the $\hat{\imath}\hat{\jmath}$ plane. In addition, we require that if the last plaquette in R is in the $\hat{\imath}\hat{\jmath}$ plane, then the newly added plaquette must increase M; it cannot be added with the same orientation as the last plaquette. This last condition rules out arrangements as in Fig. 1, with the coordinate system as shown. This rule prevents the construction of a self-avoiding sequence of plaquettes in the plane, which would make this model not solvable. The addition of plaquettes which are guaranteed to increase the maximal coordinate at

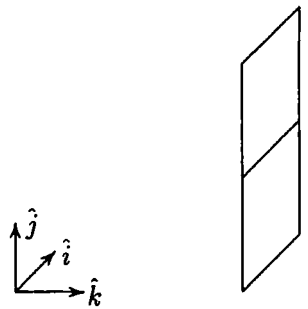

Fig. 1. Two plaquettes may not be incident if they are in the $\hat{\imath}\hat{\jmath}$ plane.

least with every second plaquette we add bestow a direction to the ribbon. In Fig. 2 we give some examples of directed ribbons. The orientation is fixed by the coordinate system in Fig. 1.

Two directed ribbons may be concatenated end to end, and a new directed ribbon is the result; since the last plaquette on the first and the first plaquette on the second may have different orientations, one extra plaquette is needed is perform the construction. If r_n is the number of directed ribbons of n plaquettes, then this construction gives

$$r_n r_m \leqslant r_{n+m+1} \tag{2.1}$$

In addition, it is easily checked that $2^n \leqslant r_n \leqslant 9^n$, so that

$$\lim_{n \to \infty} (\log r_n)/n = \log \rho \tag{2.2}$$

exists, and $2 \leqslant \rho \leqslant 9$,[10] and, moreover, $r_n \leqslant \rho^{n+1}$.

Thus, there are exponentially many directed ribbons on n plaquettes. Associate a *fugacity* x with each plaquette; then the generating function of directed ribbons is

$$g(x) = \sum_{n=1}^{\infty} r_n x^n \tag{2.3}$$

with radius of convergence ρ^{-1} and the limit $x \to \rho^{-1}$ defines a thermodynamic limit in this model. In fact, the limiting free energy per plaquette is given by $-\log \rho$.

Twist can be generated in the directed ribbon by associating a local interaction with a local orientation of three successive plaquettes which, if repeated, will form a ribbon with helical geometry. This orientation is chiral, and we consider the mirror images in Fig. 3 as left-handed or right-handed by a right-hand rule. We associate a fugacity with each of the cases in Fig. 3. In Fig. 3(a) we associate a fugacity y_L with each occurrence of this conformation in the ribbon; one may image an interaction along the dotted line between next-nearest-neighbor plaquettes giving rise to y_L. The situation in Fig. 3(b) is similarly treated, albeit with a fugacity y_R instead.

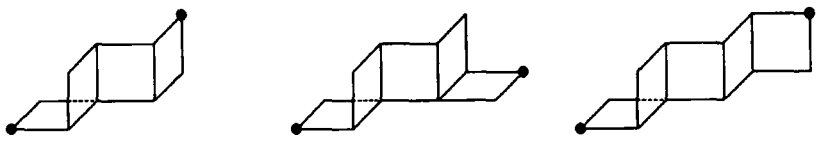

Fig. 2. Three directed ribbons, each with final plaquette in a different orientation.

(a) (b)

Fig. 3. Local conformations which contribute to twist. The conformation in (a) twists in a left-handed sense, and that in (b) in a right-handed sense. We associate fugacities y_L and y_R with (a) and (b), respectively. These fugacities may be considered as an interaction between next-nearest-neighbor plaquettes, represented by the broken lines.

We solve for the generating function of directed ribbons with these interactions. In order to do so, let $G_n(x, y_L, y_R; \sigma)$ be the canonical generating function for a directed ribbon with n plaquettes and with last plaquette in the orientation σ, where σ takes values in $\{\hat{\imath}\hat{\jmath}, \hat{k}\hat{\imath}, \hat{\jmath}\hat{k}\}$.

Consider the generating function $G_{n+1}(x, y_L, y_R; \hat{\imath}\hat{\jmath})$ for a ribbon with $(n+1)$ plaquettes: It may be obtained from $G_n(x, y_L, y_R; \sigma)$ by adding a final plaquette in the orientation $\hat{\imath}\hat{\jmath}$ onto edges with maximal $\hat{k}$ coordinates in the last plaquette. Since conformations such as in Fig. 1 may not occur, a ribbon with final plaquette in the $\hat{\imath}\hat{\jmath}$ orientation may only be constructed by adding a plaquette to ribbons with last plaquettes in either the $\hat{k}\hat{\imath}$ or $\hat{\jmath}\hat{k}$ orientations. These cases are enumerated in Fig. 4. Observe that none of these can generate one of the patterns in Fig. 3, so that there is no new twist. Associating a fugacity x with plaquettes, we conclude that

$$G_{n+1}(x, y_L, y_R; \hat{\imath}\hat{\jmath}) = 2xG_n(x, y_L, y_R; \hat{\jmath}\hat{k}) + 2xG_n(x, y_L, y_R; \hat{k}\hat{\imath}) \quad (2.4)$$

A similar analysis may be done in the other two cases; these two cases are analogous; one may be obtained from the other by interchanging $\hat{\imath}$ and $\hat{\jmath}$. The decomposition is given in Fig. 5, and it gives the recursions

$$\begin{aligned} G_{n+1}(x, y_L, y_R; \hat{k}\hat{\imath}) &= xG_n(x, y_L, y_R; \hat{k}\hat{\imath}) + 2x^2 G_{n-1}(x, y_L, y_R; \hat{k}\hat{\imath}) \\ &\quad + 2x^2(y_L + y_R)\, G_{n-1}(x, y_L, y_R; \hat{\jmath}\hat{k}) \\ G_{n+1}(x, y_L, y_R; \hat{\jmath}\hat{k}) &= xG_n(x, y_L, y_R; \hat{\jmath}\hat{k}) + 2x^2 G_{n-1}(x, y_L, y_R; \hat{\jmath}\hat{k}) \\ &\quad + 2x^2(y_L + y_R)\, G_{n-1}(x, y_L, y_R; \hat{\imath}\hat{k}) \end{aligned} \quad (2.5)$$

Finally, the generating function for a ribbon with n plaquettes is obtained by adding the three cases in (2.4) and (2.5):

$$G_n(x, y_L, y_R) = G_n(x, y_L, y_R; \hat{\imath}\hat{\jmath}) + G_n(x, y_L, y_R; \hat{\jmath}\hat{k}) + G_n(x, y_L, y_R; \hat{k}\hat{\imath}) \quad (2.6)$$

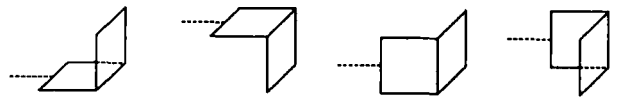

Fig. 4. The partial generating function for ribbons with final plaquette in the $\hat{\imath}\hat{\jmath}$ orientation may be obtained from the partial generating functions with one plaquette less: just add the last plaquette in the $\hat{\imath}\hat{\jmath}$ orientation. These are all the conformations which give a ribbon when the last plaquette has been added.

Since $G_n(x, y_L, y_R; \sigma)$ is a generating function for a directed ribbon with n plaquettes, it must contain a factor x^n. Define $H_n(x, y_L, y_R; \sigma) = x^{-n} G_n(x, y_L, y_R; \sigma)$, then the recursions (2.5) and (2.6) become (where we suppress the fugacities as arguments in H_n)

$$\begin{aligned} H_{n+1}(\hat{\imath}\hat{\jmath}) &= 2H_n(\hat{k}\hat{\imath}) + 2H_n(\hat{\jmath}\hat{k}) \\ H_{n+1}(\hat{\jmath}\hat{k}) &= H_n(\hat{\jmath}\hat{k}) + 2H_{n-1}(\hat{\jmath}\hat{k}) + 2(y_L + y_R)\, H_{n-1}(\hat{k}\hat{\imath}) \\ H_{n+1}(\hat{k}\hat{\imath}) &= H_n(\hat{k}\hat{\imath}) + 2H_{n-1}(\hat{k}\hat{\imath}) + 2(y_L + y_R)\, H_{n-1}(\hat{\jmath}\hat{k}) \end{aligned} \tag{2.7}$$

In order to solve these, we need some initial conditions: they are second-order relations, so we specify both $H_1(\sigma)$ and $H_2(\sigma)$. Constructing all the directed ribbons up to length 2 gives $H_1(\hat{\imath}\hat{\jmath}) = H_1(\hat{\jmath}\hat{k}) = H_1(\hat{k}\hat{\imath}) = 1$, $H_2(\hat{\imath}\hat{\jmath}) = 4$, and $H_2(\hat{\jmath}\hat{k}) = H_2(\hat{k}\hat{\imath}) = 3$. Observe that $G_n(x, y_L, y_R; \sigma) = \sum_{n=1}^{\infty} H_n(\sigma)\, x^n$, so multiply (2.7) by x^{n+1} and sum over n. Collecting terms gives

$$\begin{aligned} &G(x, y_L, y_R; \hat{\imath}\hat{\jmath}) \\ &\quad = x + 2x[\, G(x, y_L, y_R; \hat{\jmath}\hat{k}) + G(x, y_L, y_R; \hat{k}\hat{\imath})\,] \\ &G(x, y_L, y_R; \hat{\jmath}\hat{k})(1 - x - 2x^2) \\ &\quad = x + 2x^2[\, 1 + (y_L, y_R)\, G(x, y_L, y_R; \hat{k}\hat{\imath})\,] \\ &G(x, y_L, y_R; \hat{k}\hat{\imath})(1 - x - 2x^2) \\ &\quad = x + 2x^2[\, 1 + (y_L + y_R)\, G(x, y_L, y_R; \hat{\jmath}\hat{k})\,] \end{aligned} \tag{2.8}$$

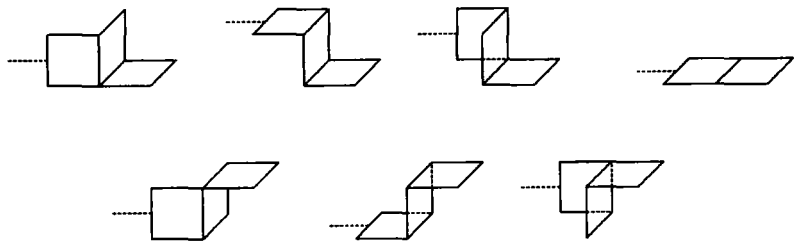

Fig. 5. The partial generating function for ribbons with final plaquette in the $\hat{k}\hat{\imath}$ or in the $\hat{\jmath}\hat{k}$ orientation may be decomposed into these seven cases.

which may be easily solved to give

$$G(x, y_L, y_R; \hat{jk}) = G(x, y_L, y_R; \hat{ki}) = \frac{(x+2x^2)[1-x-2x^2+2x^2(y_L+y_R)]}{(1-x-2x^2)^2-4x^4(y_L+y_R)^2} \tag{2.9}$$

Substituting in (2.8), we obtain the full generating function:

$$G(x, y_L, y_R) = x + \frac{2x(1+2x)^2}{(1-x-2x^2)-2x^2(y_L+y_R)} \tag{2.10}$$

3. SINGULARITY STRUCTURE AND THERMODYNAMICS

Since $G(x, y_L, y_R)$ is dependent only on x and (y_L+y_R), we put $y=(y_L+y_R)$ in (2.10). The thermodynamic limit is defined by the radius of convergence $x_c(y)$ of (2.10). Expanding (2.10) in a power series in x as

$$G(x, y) = \sum_{n=1}^{\infty} x^n H_n(y) \tag{3.1}$$

and doing a root test implies that

$$x_c(y) = \lim_{n\to\infty} [H_n(y)]^{1/n} \tag{3.2}$$

is the radius of convergence of (2.10). The quantity $[-\log x_c(y)]$ is also the limiting free energy per plaquette in the ribbon. We may compute it by finding the smallest root in te denominator in (2.10): there are two roots: $[-1\pm(9+8y)^{1/2}]/(4y+4)$. Selecting that root with minimum modulus gives the radius of convergence:

$$x_c(y) = \frac{-1+(9+8y)^{1/2}}{4y+4} \tag{3.3}$$

The shape of the phase boundary is determined by (3.3). If $y=0$, then $x_c(0)=0.5$, and for large y, $x_c(y)\sim 1/\sqrt{y}$. We plot $x_c(y)$ in Fig. 6. The noninteracting directed ribbon of Section 2 is recovered if $y_L=y_R=1$ (or $y=2$); then $x_c(2)=1/3$, and we conclude that $\rho=3$ in Eq. (2.2). If $y=0$, then the singularity in $x_c(y)$ is a double pole, but if $y>0$, then a line of simple poles is found. This line of poles is a line of branch points in the free energy.

The thermodynamic behavior of the directed lattice ribbon can be found by taking derivatives of its free energy. As an order parameter, we

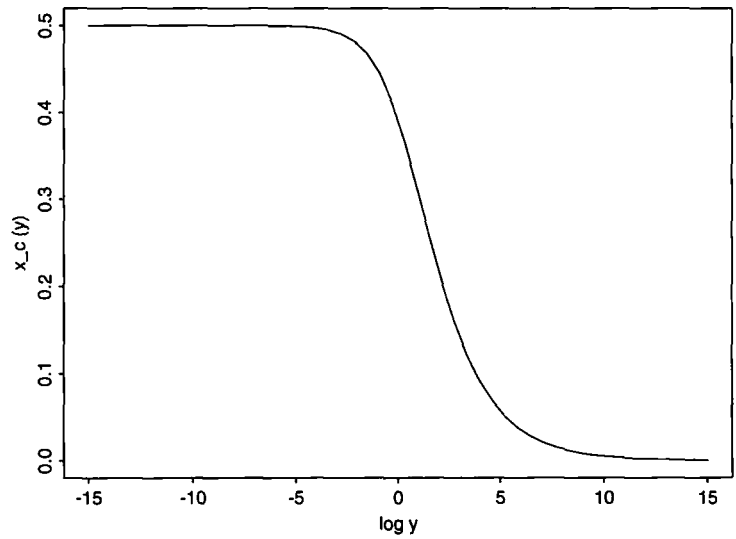

Fig. 6. The phase diagram of the directed ribbon.

define the mean *left-handed twist density* $\langle Tw_L \rangle$ of the directed ribbon to be the average number of times, per plaquette, that the pattern of Fig. 3(a) appears. This is given by

$$\begin{aligned}\langle Tw_L \rangle(y_L, y_R) &= -\frac{\partial \log x_c(y_L, y_R)}{\partial \log y_L} \\ &= \frac{y_L\{4(y_L+y_R)+5-[9+8(y_L+y_R)]^{1/2}\}}{(y_L+y_R+1)[9+8(y_L+y_R)]^{1/2}\{[9+8(y_L+y_R)]^{1/2}-1\}}\end{aligned} \tag{3.4}$$

The fugacities y_L and y_R are dependent on temperature as well as other factors (such as salinity, pH, etc.). If $y_L < 1$, then the conditions are such that there is a repulsive interaction along the dotted line in Fig. 3(a); if $y_L > 1$, then we have an attractive interaction; there is no interaction at all if $y_L = 1$. The same cases apply to y_R. (Observe that y_L will be a complicated function of temperature; for simplicit one may assume it is monotonic, but not even this is guaranteed. In any case, any connection between the real physical situation and our lattice ribbon will only be qualitative.) We assume that y_L and y_R are independent fugacities; this corresponds to the fact that left- and right-handed twists have different geometry and interaction energies in DNA.

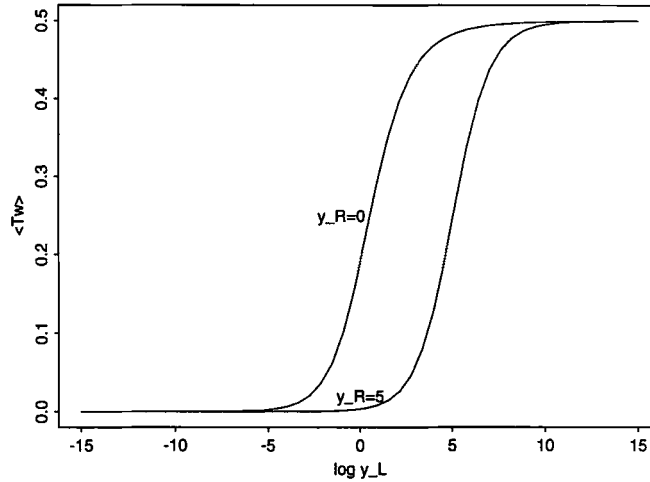

Fig. 7. The mean twist per plaquette as a function of $\log y_L$.

We plot $\langle Tw_L \rangle (y_L, y_R)$ as a function of $\log y_L$ in Fig. 7 with $y_R = 0$ and $y_R = 5$. At zero temperature, $\log y_L = +\infty$, and the ribbon is highly twisted; decreasing the fugacity y_L decreases the twist until it approaches zero for large temperatures ($y_L \to 0$). The decrease in twist is confined to an intermediate region of the scale; outside this region, changes in the fugacity do not really affect the twist in the ribbon. The dependence of $\langle Tw_L \rangle$ on y_L is best illustrated by computing the specific heat: if $y_R = 0$, then it is

$$C(y_L, 0) = \frac{\partial \langle Tw_L \rangle (y_L, y_R)}{\partial \log y_L}$$

$$= \frac{2y_L[-63 - 100y_L - 30y_L^2 + 8y_L^3 + (27 + 40y_L + 14y_L^2)(9 + 8y_L)^{1/2}]}{(y_L + 1)^2 \{[(9 + 8y_L)^{1/2} - 1]^2 (9 + 8y_L)^{1/2}\}^3} \tag{3.5}$$

We plot $C(y_L, y_R)$ in Fig. 8 for $y_R = 0$ and $y_R = 5$ (larger values of y_R do not change this picture qualitatively, it only moves the location of the peak toward larger values of y_L). There are maxima in the specific heat (if $y_R = 0$) $y_L = 1.466...$ and $y_L = 6.9064$ (if $y_R = 5$). At these maxima, the fluctuations in $\langle Tw_L \rangle$ are at a maximum, and the average size is given by the height of the peak: 0.1125... if $y_R = 0$ and 0.1192... if $y_R = 5$. At these maxima, the left-handed twist densities are 0.2320... if $y_R = 0$ and 0.2413... if $y_R = 5$. Thus, the fluctuations approach about 50% of the size of $\langle Tw_L \rangle$.

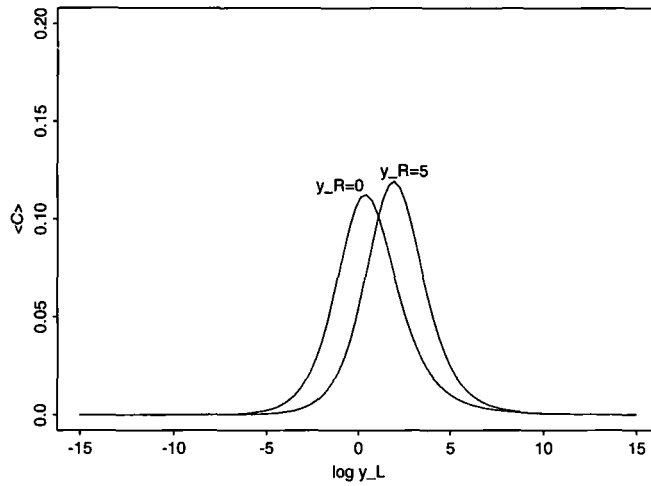

Fig. 8. The specific heat of the mean twist per plaquette.

4. CONCLUSIONS

In this paper we introduced and solved exactly a directed lattice ribbon in the cubic lattice. The crossover between a twisted (or *helical*) regime and a random (or *coiled*) regime in the ribbon is driven by changes in the fugacities y_L and y_R and caused by changes in the free energy due to conformational entropy and short-ranged local interactions (which induce twist). These are the only properties of the lattice ribbon necessary for the observed behavior. The crossover is smooth, but it mimics a phase transition in the sense that fluctuations increase in size as the crossover occurs (in this model the fluctuations in twist density approach 50% of the size of the twist). Moreover, the crossover occurs over a limited range of values of the fugacities; outside this range fluctuations are very small.

If a biopolymer such as DNA is heated in a good solvent to roughly 80°C, then the double helix is known to "melt" within a temperature range of about 10°C.[3,11] This *denaturization* of DNA is called a *helix–coil* transition in the molecular biology literature and is reversible if DNA is not heated to temperatures far above its melting temperature. Other factors, such as solvent quality (salt concentration, pH, etc.) can also denature DNA. The melting of α-helices in proteins has the same general appearance as observed for DNA.[3,11] It is believed that helices in DNA and in proteins are all due to short-ranged forces acting between repeating units along the polymer backbone.[11] The lattice ribbon model indicates that

these short-ranged forces and the conformational entropy changes which accompanies the crossover are enough to drive the helix–coil transition. The double helix in DNA is believed to be essential in maintaining the integrity of the genetic code[4] and it has to be very stable at biologically important temperatures. We observe this stability in the lattice ribbon outside the crossover regime, where fluctuations in the twist density are very small. While we expect only qualitative explanations for the helix–coil crossover behavior of DNA and other biopolymers from a model as crude as the directed lattice ribbon, there are nevertheless some advantages to this model. It is sufficiently simple to be amenable to analytic treatment, yet it has sufficient complexity to model behavior observed in DNA and other biopolymers. In particular, we believe that the behavior of the directed lattice ribbon should be interpreted as good evidence that the helix–coil transition in DNA is a crossover between two regimes primarily determined by a combination of conformational entropy and a local interaction which induces twist in the molecule.

ACKNOWLEDGMENTS

This research was supported by a grant from NSERC (Canada). We acknowledge numerous discussions with M. C. Tesi and S. G. Whittington.

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